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Chromium Colors at Low Temperatures

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CHROMIUM COLORS AT LOW TEMPERATURES

BY

CHARLES CLAFLIN RAND
MARTIN ROBERT HORNING

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CERAMICS

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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UNIVERSITY OF ILLINOIS

May 30th, 1913

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Charles Claffin Rand & Martin Robert Horning

ENTITLED Chromium Colors at Low Temperatures

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Ceramics

R. T. Stull

Instructor in Charge

APPROVED:

R. T. Stull

HEAD OF DEPARTMENT OF

Ceramics.

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In the work done by Buettner¹ and Berge² it was shown that Cr_2O_3 imparts a green color to the glaze when it functions basic and red when it functions acid. Buettner's red chromium glaze was

.9 PbO)
 .1 K_2O) .2 Cr_2O_3 (.6 SiO_2 . He gives the limiting SiO_2 con-

tent as one equivalent and states that small amounts of Al_2O_3 do not affect the color. Berge gives a brick red, PbO) .15 Al_2O_3 (0.6 SiO_2
 .05 Cr_2O_3

and as a brilliant red, PbO) .1 Al_2O_3 (0.6 SiO_2
 .05 Cr_2O_3

Our investigations were carried out for the purpose of confirming these limits or determining new ones. Also, to determine the effect of replacing part of the lead by calcium, magnesium, barium, and zinc.

Group I.

In this group the RO and Al_2O_3 remain constant, the SiO_2 and Cr_2O_3 being variables. The limits covered were:

PbO) 0.1 Al_2O_3 (0.5 to 1.9 SiO_2
) .02 to 0.2 Cr_2O_3 (

Fifty-six glazes were made, the horizontal series being designated by letters and the vertical series by numbers. The members of the group were made by blending the four corner glazes according to their combining weights. The formulae and batch weights of the four corners are:

Formulae					Batch Weights			
	PbO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	Pb ₃ O ₄	China clay #7	Cr ₂ O ₃	Flint
I A 1	1	0.1	0.02	0.5	228	25.8	3.06	18
I A 8	1	0.1	0.02	1.9	228	25.8	3.06	102
I G 1	1	0.1	0.2	0.5	228	25.8	30.6	18
I G 8	1	0.1	0.2	1.9	228	25.8	30.6	102

The four batches were made from materials passed through a 20 mesh sieve, ground wet for two hours and passed through a 120 mesh sieve. The glazes were applied to two sets of trial pieces. One set consisted of 2" discs of the following composition:

Georgia Kaolin 10 parts
 English China Clay #7, 25 parts
 English Ball Clay 15 parts
 Flint 25 parts
 Potash spar 25 parts

The other set were 2" discs made from Bloomingdale stoneware clay. The trial pieces were previously biscuitied to cone 5. The glazes low in flint cracked somewhat in drying but not enough to

be serious. The trials were placed in wadded saggers and burned in an open fire down draft kiln (Fig. 1), in sixteen hours, coal being used as fuel. When the temperature as indicated by the pyrometer was 880°C , cone 010 went down and the fires were drawn. The kiln was allowed to cool slowly, the damper being closed. The results from this burn were not of much value. All the glazes were green or greenish yellow on account of the long heat treatment near the finishing temperature. The glaze when in a fluid condition attacked the body and took up SiO_2 , thus increasing its acidity, under which condition Cr_2O_3 gives green, as is shown by later results.

The glazes were applied to a similar set of trial pieces and burned to cone 010 in five hours, although when the cone went down the pyrometer showed a temperature of only 900°C . This behaviour of the cones is probably due to reducing conditions. The cones fell over due to bloating at the base and were not fused. The kiln was cooled slowly as before.

Owing to the fact that the glazes were not applied thickly enough and that they were slightly underburned, it is difficult to draw many conclusions as to their true character. The results of the stoneware trials were discarded entirely, since the body was too easily attacked by the glaze. On the porcelain trials where the glaze was thin a green or yellowish green color resulted. All the trials were green around the edge where the glaze was thin. Also on trials where a portion of the glaze had flaked off, a greenish yellow film was visible next to the body. Two vases which had been dipped in glaze I A 1 came out a lemon yellow

Fig. 1.

4.

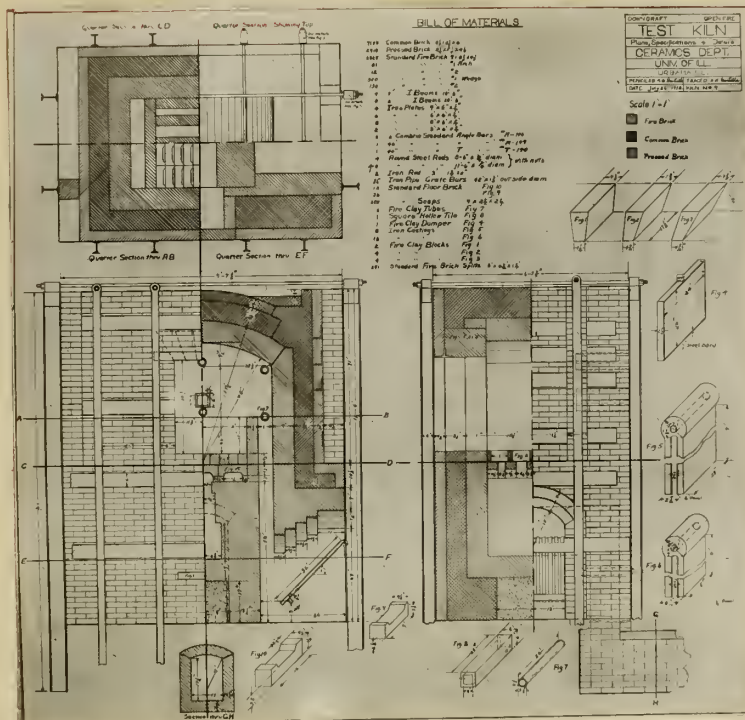
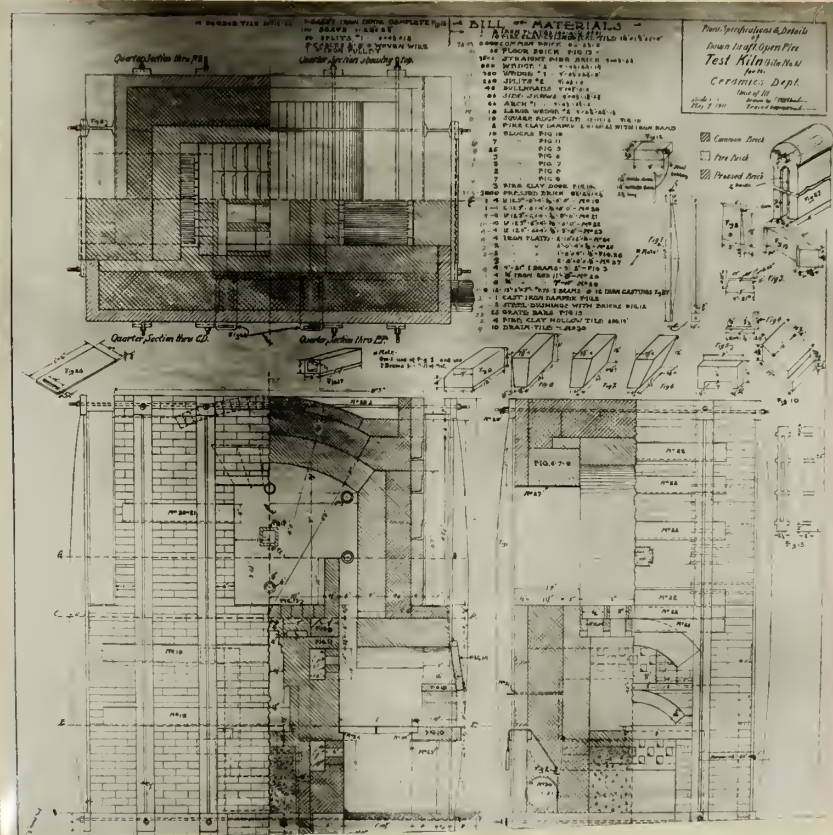


Fig. 2.



color instead of the orange which showed on the corresponding trials. This was due to the fact that most of the glaze had run off and left only a thin coating. An attempt has been made below to describe the color of the glazes (Fig. 3). The texture is shown in the accompanying photograph (Fig. 4).

The glazes were next applied in a thicker coat to biscuited wall tile. They were burned to a temperature of 950° in five hours and cooled slowly as before. An open fire down draft kiln (Fig. 2) was used, with coke as fuel. Fairly good results were obtained from this burn and the conclusions drawn were as follows: (See Figs. 5 and 6).

Increasing Cr_2O_3 increases redness up to .17 Cr_2O_3 . Beyond this point more Cr_2O_3 is present than can combine to form the red color, in which case the excess produces its natural green and makes the resulting color reddish brown. This is shown in glazes D1, E1, F1, and G1, all of which show increasing redness except G1 which is a reddish brown. At 950°C from .11 to .14 Cr_2O_3 seems to be the high limit, but .17 Cr_2O_3 with low SiO_2 produced a good dark red at 1050°C .

1.3 SiO_2 seems to be the highest SiO_2 content at which a good red can be produced, as the glazes higher in SiO_2 were green or greenish red even when mature. The glazes containing less than 1.3 SiO_2 , which were green when immature, turned red when burned 100° higher.

The best red glaze at 950°C is I D 4, with the composition

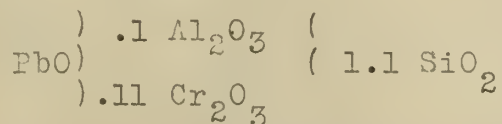
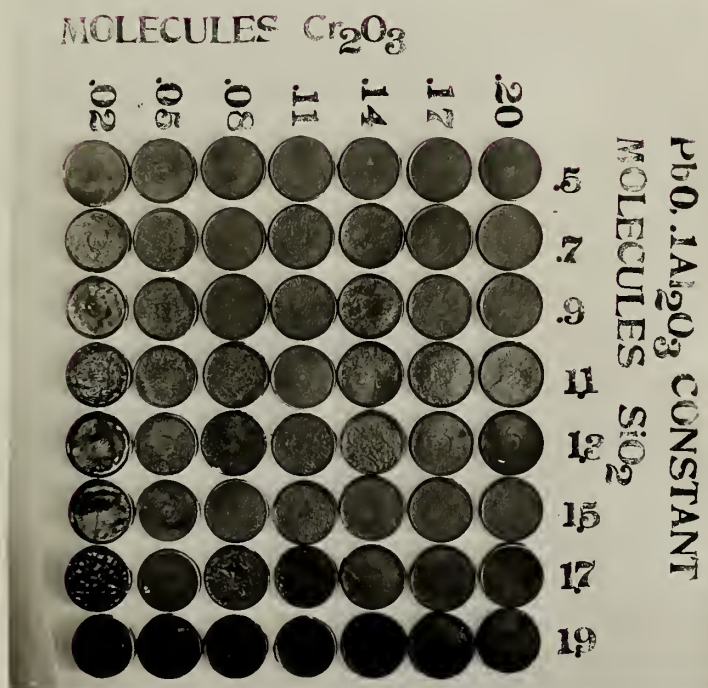


Fig.
3

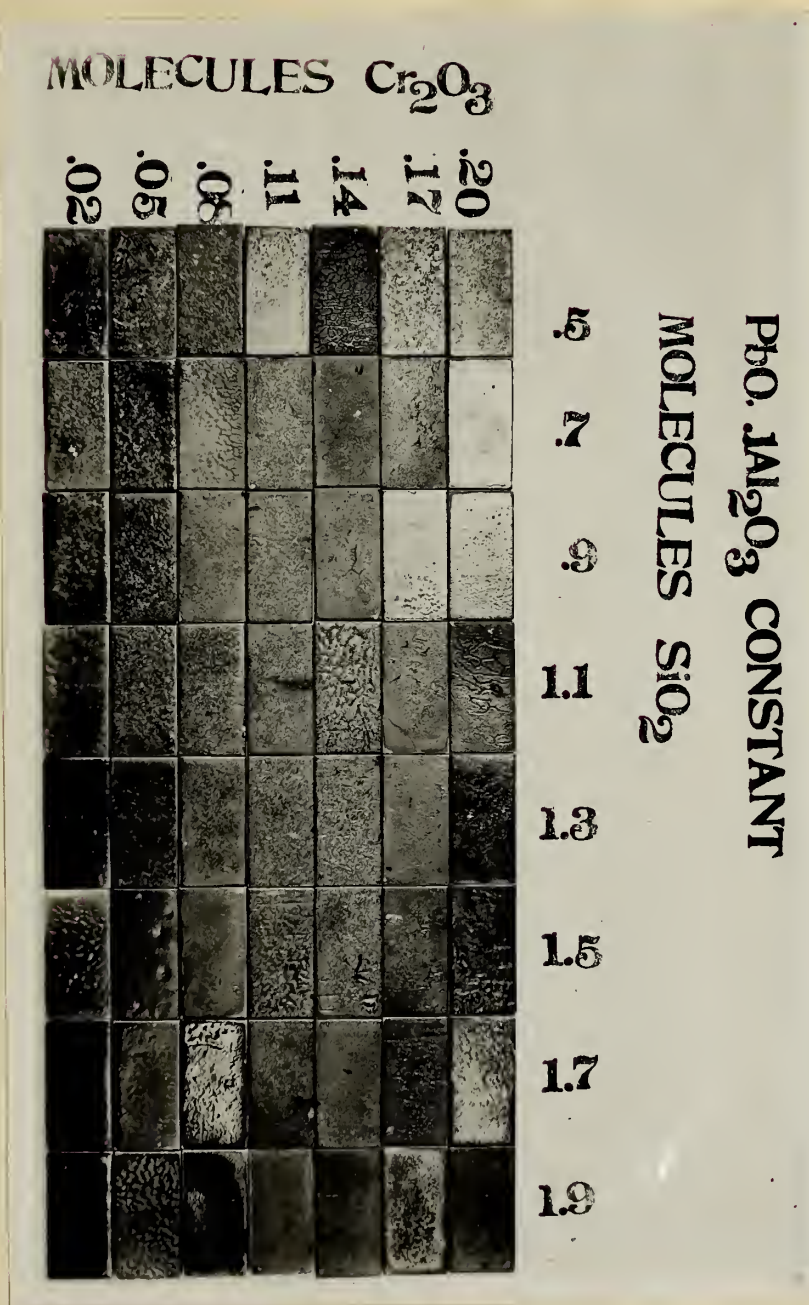
	1	2	3	4	5	6	7	8
G	Green	Green	Green	Reddish green Crystals	Green	Green	Green	Green
F	Reddish Brown	Green	Dirty Red	Dirty Red	Dirty Red	Green with Red	Greenish Red	Greenish Red
E	Greenish Brown	Dirty Red Crystals	Dirty Red Crystals	Dirty Red Crystals	Greenish Red	Greenish Red	Greenish Red	Greenish Red
D	Greenish Brown	Red Crystals	Brownish red with Green Crystals	Brownish red with Green Crystals	Brownish red with Green Crystals	Brownish red with Green Crystals	Green	Green
C	Brownish	Brownish	Brownish with Crystal	Dirty Red Crystals	Dirty Red Crystals	Green with red Crystals	Green with red Crystals	Green with red Crystals
B	Light red Crystals	Yellowish red Crystals	Yellowish red Crystals	Yellowish red Crystals	Yellowish red Crystals	Yellowish Red crystals	greenish yellow	Light red with Green
A	Orange large Crystal	Orange with red crystals	Dirty yellowish crystals	Greenish yellow Crystals	Greenish Yellow	Greenish Yellow	Yellowish Green	Light Green

Fig. 4.



	1	2	3	4	5	6	7	8
G	Reddish Green dark	Reddish Green dark	Reddish Green dark	Reddish Green dark	Reddish Green dark	Reddish Green dark	Reddish Green dark	Reddish Green dark
F	Light Reddish Green	Light Reddish Green	Light Reddish Green	Light Reddish Green	Light Reddish Green	Light Reddish Green	Light Reddish Green	Light Reddish Green
E	Brownish Crystals	Brownish Few Crystals	Brownish. Few Crystals	Greenish Red. Few Crystals	Greenish Red Few Crystals	Greenish Red Few Crystals	Light Reddish Green. Few Crystals	Light Reddish Green. Few Crystals
D	Good Red. Crystals	Good Red. Crystals	Good Red. Crystals	Good Red. Crystals	Good Red. Crystals	Greenish Red Crystals	Greenish Red Crystals	Nearly Green
C	Light Red Crystals	Mixed Red & Green. Crystals	Mixed Red & Green. Crystals	Mixed Red & Green. Crystals	Mixed Red & Green. Crystals	Yellowish Green Crystals	Green Crystals	Green
B	Yellowish Red. Crystals	Yellowish Red. Crystals	Yellowish Red. Crystals	Greenish Red. Crystals	Greenish Red. Crystals	Greener Crystals	Greener Crystals	Green with Yellow
A	Crystals	Crystals	Orange with Crystals	increasing Crystals	yellow Crystals			Lemon Yellow

Fig. 6.



Group II.

In this group the PbO and Cr_2O_3 remained constant, the SiO_2 and Al_2O_3 being variables. The limits covered were:

$$\begin{array}{l} \text{PbO} \quad \left. \begin{array}{l}) \text{ 0 to 0.21 } \\) \text{ 0.12 } \end{array} \right\} \begin{array}{l} \text{Al}_2\text{O}_3 \\ \text{Cr}_2\text{O}_3 \end{array} \quad \left(\begin{array}{l} \\ \end{array} \right. \left. \begin{array}{l} \\ \end{array} \right\} \begin{array}{l} \text{SiO}_2 \\ \end{array} \left(\begin{array}{l} \text{0.5 to 1.9} \\ \end{array} \right.$$

Fifty-six glazes were made in this group, the horizontal series being designated by letters and the vertical series by numbers. The members were made by blending the four corners as in Group I. The formulae and batch weights of the four corners are:

	Formulae				Batch weights			
	PbO	Al_2O_3	Cr_2O_3	SiO_2	Pb_3O_4	China clay #7	Cr_2O_3	Flint
II A 1	1	0	0.12	0.5	228	—	18.36	30
II A 8	1	0	0.12	1.9	228	—	18.36	114
II G 1	1	0.21	0.12	0.5	228	54.18	18.36	4.8
II G 8	1	0.21	0.12	1.9	228	54.18	18.36	88.8

The glazes were prepared and applied to trial pieces similar to those in Group I and a set of these glazes was burned with each set of Group I.

First Burn. The results obtained in this burn were unsatisfactory for the same reasons which apply to Group I.

Second Burn. (See Figs. 7 and 8) Most of the glazes obtained from this burn were underfired. In the bottom row the glazes are all immature. In the next two rows the glazes are more

	1	2	3	4	5	6	7	8
G	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Green	Green	Green	Green
F	Greenish Red	Greenish Red	Greenish Red	Green	Green	Green	Green	Green
E	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Green	Green	Green
D	Brownish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Green	Green	Green
C	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Brownish Red	Brownish Red	Brownish Red	Brownish Red
B	Red Crystals	Greenish Red	Brownish Red	Brownish Red	Brownish Red	Good	Good	Good
A	Red Crystals	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Brownish Red	Brownish Red	Brownish Red

mature. This is probably due to the slight increase of Al_2O_3 which, when added in small amounts lowers the temperature of fusion which is in confirmation of the findings of Purdy¹ and Orton² in regard to small additions of Al_2O_3 .

Up to 0.1 Al_2O_3 increase of that constituent makes the glaze darker red above that point the glazes are all immature except in the upper right hand corner, where there is a better balance of Al_2O_3 and SiO_2 . These glazes would show some red if burned higher as is shown by the next burn of this group.

Below .07 Al_2O_3 increase in SiO_2 seems to improve the color and texture of the glaze. Above this point increase in SiO_2 increases greenness and beyond 1.3 SiO_2 practically no red shows.

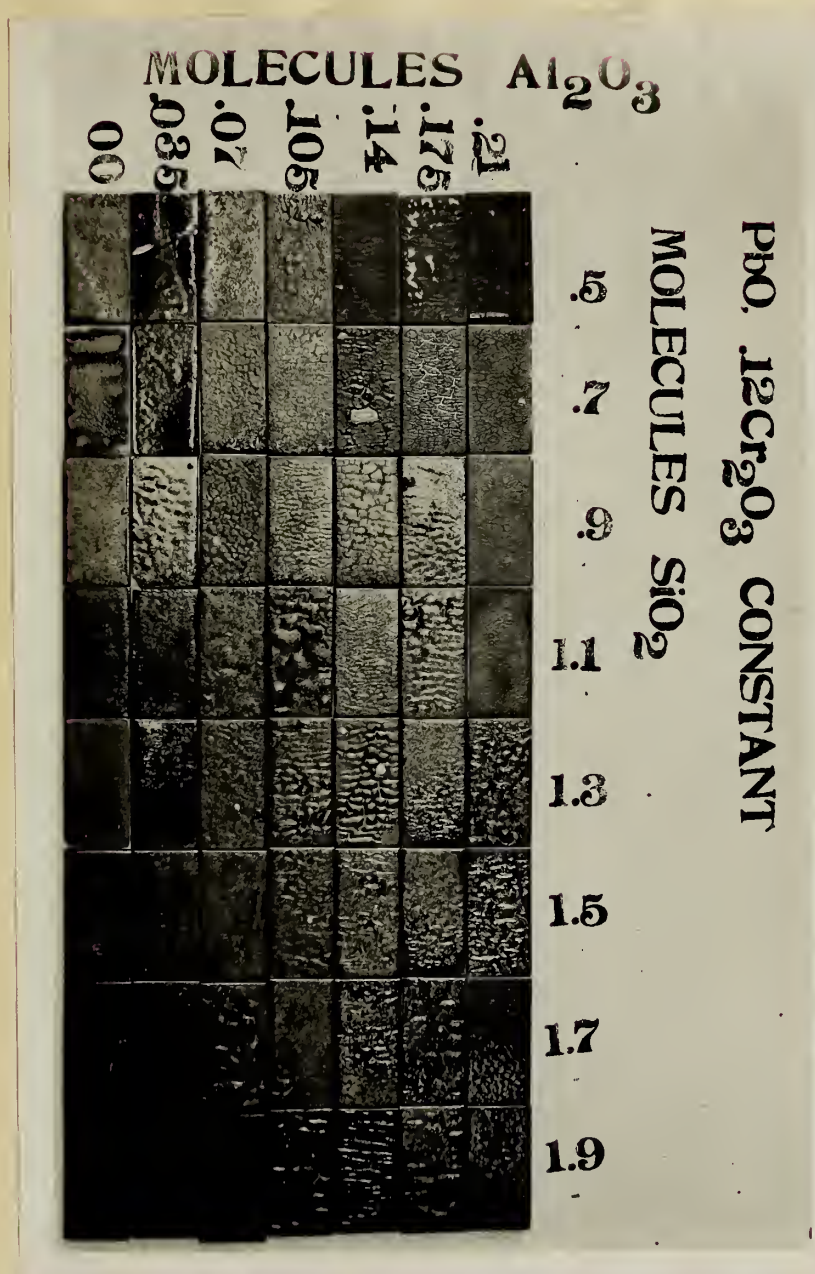
Third Burn. (See Figs. 9 and 10) Most of the glazes appear to be mature or nearly so. In the bottom row increase of SiO_2 increases the fusion temperature of the glaze the last four glazes being slightly underfired and tending toward green. Glaze II A 4 is a peculiar golden brown color with many small crystals. In the next two rows the high SiO_2 glazes seem to be the best. II B 8 resembles II A 4 closely the golden color being a little more pronounced. Above .07 Al_2O_3 increase of SiO_2 increases greenness though red crystals occur in all the glazes. The fact that the glazes in the upper right hand corner show a good red in spots in spite of high SiO_2 is due to the high content

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1. T. A. C. S. Vol. 4 p. 67

2 .T. A. C. S. Vol. 5 p. 13

	1	2	3	4	5	6	7	8
G	Brownish Red	Brownish Red	Brownish Red	Green		Reddish Green Green increasing	Green	
F	Brownish Red	Brownish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red Green increasing	Greenish Red	Greenish Red
E	Brownish Red	Brownish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red Green increasing	Greenish Red	Greenish Red
D	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Greenish Red	Greenish
C	Greenish Red. Crystals	Greenish Red. Crystals	Greenish Red. Crystals	Greenish Red. Crystals	Greenish Red. Crystals	Greenish Red. Crystals	Greenish Red.	Greenish Red.
B	Greenish Red Crystals	Greenish Red Crystals	Greenish Red Crystals	Greenish Red Crystals	Brownish Red	Brownish Red Brown increasing	Brownish Red	Brownish Red
A	Red Crystals	Greenish Red Crystals	Greenish Red Crystals	Brownish Red	Brownish Red	Brownish Red Brown increasing	Brownish Red	Brownish Red

Fig. 10.



Molecules.

Batch Weights.

PbO		Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	Pb ₃ O ₄	China clay #7	Cr ₂ O ₃	Flint		ID4
1		.1	.11	1.1	228	25.8	16.83	54		

PbO	CaO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	Pb ₃ O ₄	Whiting	China clay #7	Cr ₂ O ₃	Flint	A
.5	.5	.1	.11	1.1	114	50	25.8	16.83	54	

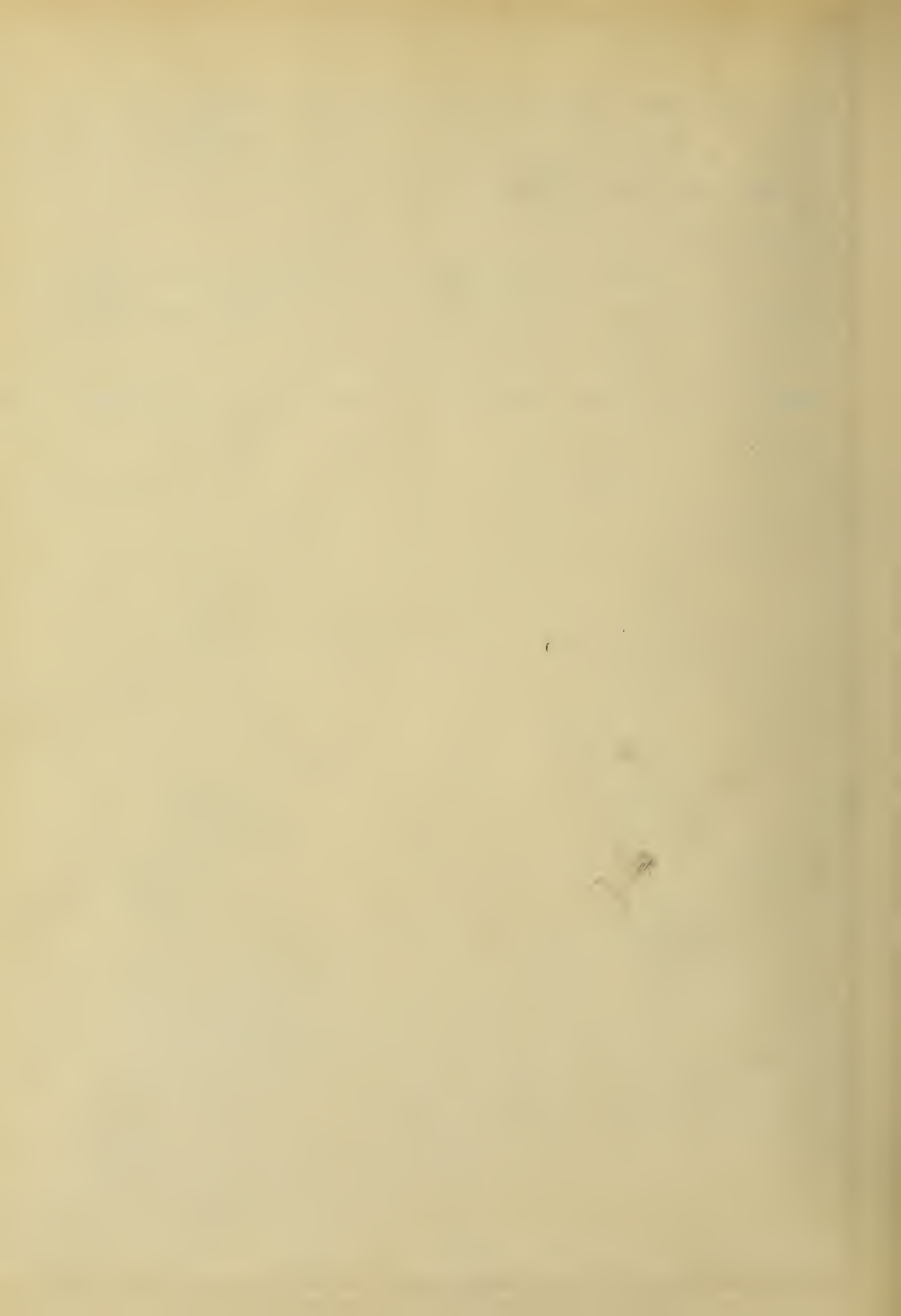
PbO	MgO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	Pb ₃ O ₄	MgCO ₃	China clay #7	Cr ₂ O ₃	Flint	B
.5	.5	.1	.11	1.1	114	42	25.8	16.83	54	

PbO	BaO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	Pb ₃ O ₄	BaCO ₃	China clay #7	Cr ₂ O ₃	Flint	C
.5	.5	.1	.11	1.1	114	98.5	25.8	16.83	54	

PbO	BaO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	Pb ₃ O ₄	ZnO	China clay #7	Cr ₂ O ₃	Flint	D
.5	.5	.1	.11	1.1	114	40.5	25.8	16.83	54	

The glazes were prepared in the same manner as in Groups I and II applied to biscuited wall tile and burned to 950°C in seven hours. An open fire down draft kiln (Fig. 2) was used with coke as fuel. The kiln was cooled slowly.

The results obtained were very unsatisfactory. All of the glazes containing more than .05 of the replacing metal crawled very badly. The two glazes which contained .05 CaO and .05 ZnO respectively showed a good red color but were no improvement over I D 4.



Conclusions.

From the results obtained the following conclusions may be drawn:

1. That the red color is produced when Cr_2O_3 functions acid, which confirms the results of Buettner and Berge.
2. That 1.3 equivalent is the highest SiO_2 content at which a good red can be produced, with .1 Al_2O_3 constant.
3. That red may be produced above 1.3 SiO_2 , providing enough Al_2O_3 is present to cause the Cr_2O_3 to function acid.
4. That below 1.3 SiO_2 , with .1 Al_2O_3 constant, increase of Cr_2O_3 increases redness up to .2 equivalent.
5. That with .12 Cr_2O_3 constant, increase of Al_2O_3 above .07, darkens the red color.
6. That with .5 to 1.9 SiO_2 , .12 Cr_2O_3 constant, increase of Al_2O_3 up to .07 lowers the maturing temperature of the glaze.
7. That when .05 PbO is replaced by .05 CaO , BaO , MgO , or ZnO , the red color is but slightly effected.
8. That when more than .05 CaO , BaO , MgO or ZnO is used, the red color is destroyed.

Above .05 CaO gives brown.

Above .05 MgO gives brown.

Above .05 BaO gives brown tending toward yellow.

Above .05 ZnO gives greenish brown.





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